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An Electrolyte for Low-Temperature Applications of Lithium and Lithium-Ion Batteries

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Abstract

An electrolyte consisting of a 1.0-molar solution of lithium hexafluorophosphate (LiPF_6) in 1:1:1 ethylene carbonate (EC)-dimethyl carbonate (DMC)-ethyl methyl carbonate (EMC) is proposed for low-temperature applications. The new electrolyte has good conductivity and electrochemical stability. Lithium and lithium-ion cells using the new electrolyte were found to be operable at temperatures down to -40°C .

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Introduction

Various Army missions require lithium and lithium-ion batteries that can operate at temperatures down to -40°C . Because the electrolytes presently used in commercial lithium-ion batteries freeze at about -30°C , considerable attention is being given to finding cosolvents for these electrolytes to increase their liquidus range. Recently, ethyl methyl carbonate (EMC) was found to be a useful cosolvent¹⁻³ in binary solutions with propylene carbonate (PC) and ethylene carbonate (EC), because of its low freezing point (-55°C). In this study, we used EMC as a cosolvent with EC and dimethyl carbonate (DMC) in ternary solutions to increase the liquidus range of the lithium-ion battery electrolyte. Thus, Li/LiCoO₂ and graphite/LiCoO₂ button cells that use a 1.0-molar solution of lithium hexafluorophosphate (LiPF₆) in 1:1:1 EC-DMC-EMC as the electrolyte were found to be operable at temperatures down to -40°C . Further, the new electrolyte was found to have good conductivity, as well as good electrochemical stability. The results are summarized in this report.

Experimental Procedure

LiPF₆ (from Hashimoto, Japan) and SFG-44 graphite (from Timcal) were used as received. EC, DMC, and EMC (all from Grant Chemicals) were dried over molecular sieves before use. Lithium foil (20 mil thick, from the Cypress-Foote Mineral Company), packed over argon, was opened in an argon-filled dry box (from the Vacuum Atmosphere Company) with a moisture content of less than 0.5 ppm.

The electrolyte conductivities were measured with a Wayne Kerr model 6425 precision bridge at a frequency of 1 kHz in sealed Jones-type conductivity cells. Cell constants were determined by a standard KCl solution. An environmental chamber (manufactured by Tenney, Jr.) controlled the temperature for the conductivity and cell studies.

We fabricated lithium and lithium-ion cells using a 1.0-molar solution of LiPF₆ in 1:1:1 EC-DMC-EMC in a button cell configuration. The cell component specifications and button cell assembly details have been described previously.⁴ All electrode disks were 0.51 mm thick and 15.7 mm in diameter. Lithium electrodes were cut from a lithium foil and pressed onto nickel screen (Exmet 5 Ni 6-3/0A). Graphite electrodes with a theoretical capacity of 24 mAh were fabricated with the use of 10 wt.%

¹M. Ue and S. Mori, "Mobility and ionic association of lithium salts in propylene carbonate-ethyl methyl carbonate mixed solvents," *J. Electrochem. Soc.* **142**, 2577 (1995).

²Y. Ein-Eli, S. R. Thomas, V. Koch, D. Aurbach, B. Markovsky, and A. Schechter, "Ethylmethylcarbonate, a promising solvent for Li-ion rechargeable batteries," *J. Electrochem. Soc.* **143**, L273 (1996).

³Y. Ein-Eli and V. R. Koch, "Li-ion battery electrolytes formulated for low temperature applications," *Proceedings of the Workshop for Battery Exploratory Development*, pp 253-259, Burlington, VT (July 1997).

⁴E. J. Plichta and S. Slane, "Conductivity of lithium imide in mixed aprotic solvents for lithium cells," *J. Power Sources* **69**, 41 (1997).

PTFE (Teflon) binder. The electrode mixture was spread on a copper foil current collector. We made lithium cobalt oxide electrodes with a theoretical capacity of 42 mAh by mixing 80 wt.% LiCoO_2 with 10 wt.% Vulcan CX-72R carbon and 10 wt.% PTFE and spreading the paste on an aluminum screen current collector. The cells were fabricated with a Celgard 2402 separator (0.05 mm thick and 1.9 cm in diameter). The cells were cycled by an Amel model 546 galvanostat/electrometer, and the currents applied to the cell were verified with a Fluke model 8640A digital multimeter. We performed voltammetric scans using an EG&G PAR potentiostat/galvanostat (model 273). The experiments were computer-controlled with the use of EG&G PAR electrochemical analysis software (model 270).

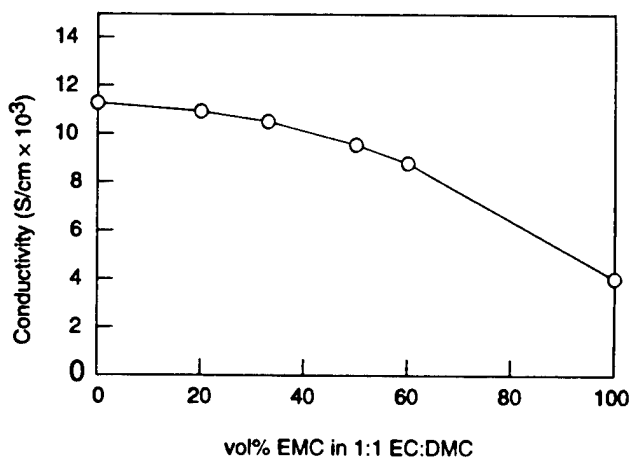
Results and Discussion

The electrolyte in commercial lithium-ion cells generally consists of a 1.0-molar solution of LiPF_6 in 1:1 EC-DMC (50:50 vol.%). The electrolyte freezes at about -30°C , so the commercial lithium-ion cells cannot be used in several military applications that require operation at lower temperatures. We have, therefore, employed EMC as a cosolvent to increase the liquidus range of the electrolyte used in commercial cells.

The conductivities of 1.0-molar solutions of LiPF_6 in 1:1 EC-DMC containing 0 to 100 vol.% EMC were measured at 25°C , and the data are plotted in figure 1. It is seen that the electrolyte conductivity decreases from ~ 0.011 to ~ 0.004 S/cm as the concentration of EMC is increased from 0 to 100 vol.%. However, the decrease in electrolyte conductivity is only minimal in the initial stages, and the conductivity of a 1.0-molar solution of LiPF_6 in 1:1:1 EC-DMC-EMC is close to the conductivity in a 1:1 EC-DMC solution.

We found the freezing point of a 1.0-molar solution of LiPF_6 in 1:1:1 EC-DMC-EMC to be approximately -50°C compared to the freezing point of approximately -30°C for the electrolyte using a 1:1 EC-DMC, binary solvent mixture. The conductivities of 1.0-molar solutions of LiPF_6 in EMC, 1:1 EC-DMC, and 1:1:1 EC-DMC-EMC were also measured in the

Figure 1.
Conductivities of
1.0-molar solutions
of LiPF_6 in ternary
solvent mixture
EC-DMC-EMC as
function of
percentage volume
of EMC at 25°C .



temperature range of $-40\text{ }^{\circ}\text{C}$ to $55\text{ }^{\circ}\text{C}$. The data are plotted in figure 2 as a function of temperature.

The conductivities of the EMC solutions at all temperatures are too low to consider these solutions as electrolytes for lithium or lithium-ion batteries. However, EMC can be used as a cosolvent for the commercial electrolyte consisting of a 1.0-molar solution of LiPF_6 in 1:1 EC-DMC to increase its liquidus range. The conductivities of the electrolyte using the ternary solvent mixture are, however, slightly lower at temperatures above $-20\text{ }^{\circ}\text{C}$ (fig. 2) compared to the conductivities of electrolytes using the binary solvent mixture.

The electrochemical stabilities of solutions of LiPF_6 in EMC, 1:1 EC-DMC, and 1:1:1 EC-DMC-EMC were examined by recording linear sweep voltammograms at smooth glassy carbon electrodes (electrode area: 0.0792 cm^2). Typical voltammograms obtained at a scan rate of 20 mV/s are presented in figure 3. It is seen that all three solutions are electrochemically stable up to a potential of about 4.5 V , although the anodic currents in EMC solutions are much smaller than those observed in the EC-DMC and EC-DMC-EMC solutions.

Figure 2.
Conductivities of 1.0-molar solutions of LiPF_6 in EMC (Δ), 1:1 EC-DMC (\circ), and 1:1:1 EC-DMC-EMC (\square) as function of temperature.

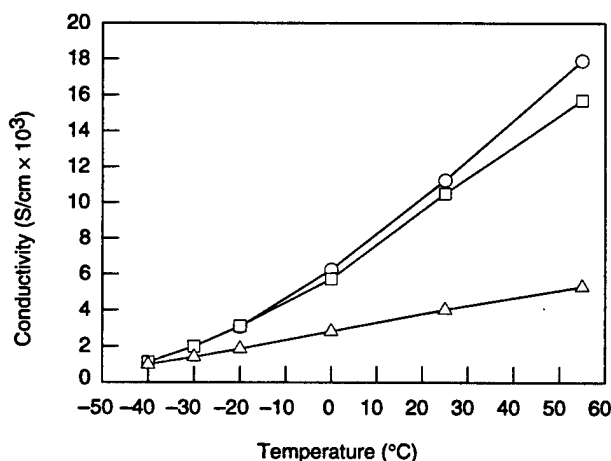
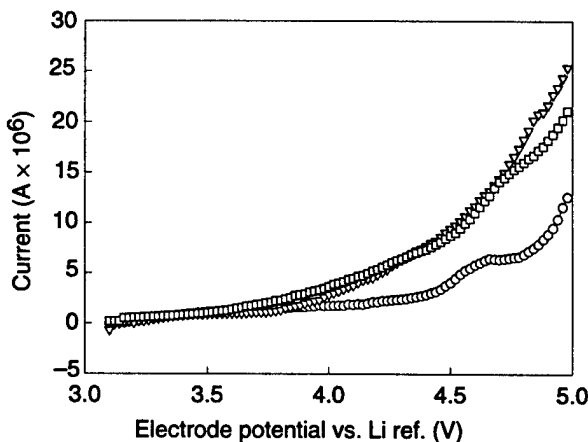


Figure 3. Linear sweep voltammograms obtained at glassy carbon electrode at scan rate of 20 mV/s in 1.0-molar solutions of LiPF_6 in EMC (\circ), 1:1 EC-DMC (Δ), and 1:1:1 EC-DMC-EMC (\square).



The new electrolyte was evaluated in the following cells:

Li/electrolyte/SFG-44 graphite (I)

Li/electrolyte/LiCoO₂ (II)

SFG-44 graphite/electrolyte/LiCoO₂ (III)

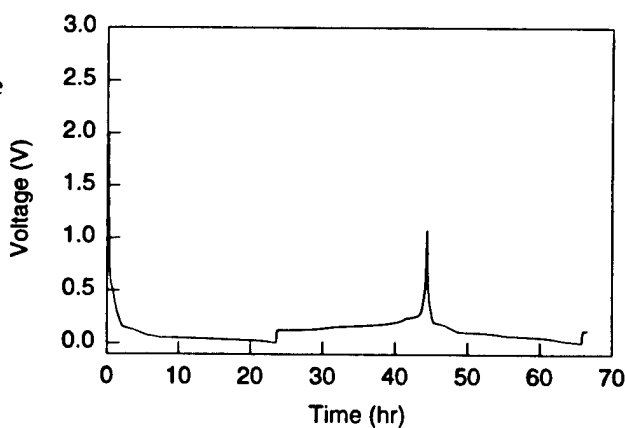
Cell I was used to determine the reversible and irreversible capacity of the graphite electrode in button cells. The cell was discharged at a constant current of 1 mA to 0.01 V, which resulted in the intercalation of lithium into graphite. The total cell reaction may be represented as



The cell was then cycled between the voltage limits of 0.01 and 1.5 V, and the voltage-time plots for the first discharge and the following charge-discharge cycle are shown in figure 4. This plot is similar to plots observed by other workers for lithium/graphite cells using nonaqueous electrolytes.^{3,5} The capacities of the graphite electrode during the initial discharge and the following charge-discharge cycle were found to be 354.4, 322.7, and 323.9 mAh/g, respectively. Thus, the irreversible capacity during the first discharge was ~31.7 mAh/g. After the initial discharge, the capacity of the graphite electrode was found to be approximately the same for the charge and discharge cycles.

The reversible capacity of ~323 mAh/g for the graphite electrode was found to be comparable to the capacity reported by other workers⁵ for graphite electrodes.

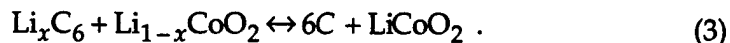
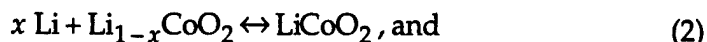
Figure 4. Typical voltage-time curve for cell I for first discharge and following charge-discharge cycle at constant current of 1 mA using 1.0-molar solution of LiPF₆ in 1:1:1 EC-DMC-EMC as electrolyte.



³Y. Ein-Eli and V. R. Koch, "Li-ion battery electrolytes formulated for low temperature applications," *Proceedings of the Workshop for Battery Exploratory Development*, pp 253-259, Burlington, VT, July 1997.

⁵S. Megahed and B. Scrosati, "Lithium-ion rechargeable batteries," *J. Power Sources* 51, 79 (1994).

Cells II and III were used to study the performance of the lithium and lithium-ion cells at different temperatures using a 1.0-molar solution of LiPF_6 in 1:1:1 EC-DMC-EMC as the new electrolyte. The cell reactions in cells II and III, respectively, may be represented as



Both cells II and III were assembled in the discharged state and were first charged to a voltage of 4.15 V at a constant current of 1 mA. The discharge curves obtained at 25 °C, -20 °C, and -40 °C at a constant discharge current of 1 mA for cells II and III are presented in figures 5 and 6.

It can be seen that both cells II and III are operable at temperatures down to -40 °C. The capacity of the lithium-ion cell (fig. 6) at -40 °C was, however, found to be only a fraction of the capacity obtained at 25 °C. This may be attributed to the poor performance of the graphite-lithium anode at -40 °C, since the capacity of the lithium cell (fig. 5) at the same temperature was found to be about 52 percent of the capacity obtained at 25 °C.

Figure 5. Typical discharge curves for cell II at constant current of 1 mA at various temperatures using 1.0-molar solution of LiPF_6 in 1:1:1 EC-DMC-EMC as electrolyte.

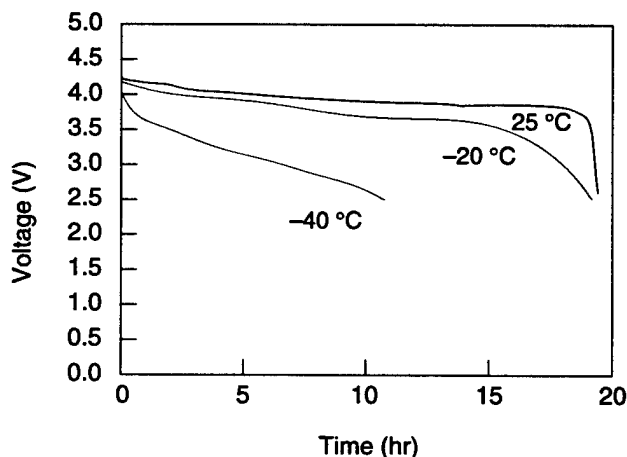
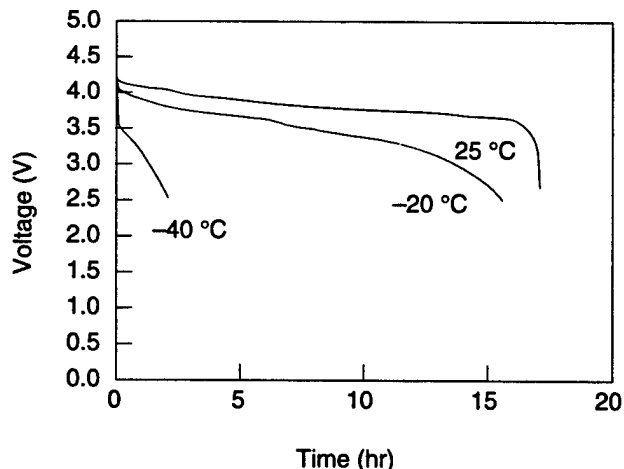


Figure 6. Typical discharge curves for cell III at constant current of 1 mA at various temperatures using 1.0-molar solution of LiPF_6 in 1:1:1 EC-DMC-EMC as electrolyte.



Conclusions

Ethyl methyl carbonate was found to be a useful cosolvent to increase the liquidus range of the LiPF_6 solutions in 1:1 EC-DMC at low temperatures. Thus, a 1.0-molar solution of LiPF_6 in 1:1:1 EC-DMC-EMC was found to possess good conductivity and electrochemical stability. Lithium and lithium-ion cells using the new electrolyte were found to be operable at temperatures down to $-40\text{ }^\circ\text{C}$.

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